SCIENTIFIC AND TECHNICAL REPORT ON

"Temperature Effects on Chemical Structure and Motion in Coal"

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Introduction

As described in previous reports, the effects of moderate temperatures (up to 230 °C) is to increase molecular/macromolecular mobility in coals, as determined by ^1H CRAMPS measurements, especially dipolar-dephasing experiments. Pyridine-saturated coals have also been studied with the same kinds of NMR experiments. We found that thermal activation and solvent saturation promote the molecular mobility of coals in quite different ways. Our results have provided some new insight into the molecular/macromolecular structure and dynamics of coals. In this report, we compare ^1H CRAMPS results obtained on the original (untreated) Argonne Premium coal 601 with those obtained on the pyridine extraction residue of coal 601. These results are consistent with our previous results and provide further information on the structure and dynamics of coals.

Results and Discussion

The pyridine extraction residue of coal 601 was obtained from the residue of the Soxhlet extraction and was dried in a vacuum oven at 120 °C for two days. Variable-temperature dipolar-dephasing ^1H CRAMPS experiments were carried out on the dry residue. Figure 1B shows a set of dipolar dephasing spectra of the dry residue obtained at a measuring temperature of

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25 °C. A linear combination of two Gaussian decays was used to model the dipolar-dephasing curve of this extraction residue. The results obtained from this analysis model are presented in Table 1. For comparison, the corresponding dipolar-dephasing results obtained on the original coal 601 are listed in Table 2, and the dipolar dephasing spectra of the original coal 601 are illustrated in Figure 1A.

Several features can be readily seen from Figure 1 and Tables 1 and 2.

- (1) The ratio of the aliphatic component to the aromatic component is lower in the residue than in the original coal. This is consistent with the expectation that the aliphatic component is predominant in the pyridine extract.
- (2) The time constants of the fast-decay components are mainly in the 9-16 μ s range (for all temperatures) for both the original coal and the extraction residue. The time constants of the slow decay components of the residue are 46-76 μ s, a little bit longer than those of the original coal. However, the fractions of the fast decay component in the residue are much higher than those of the original coal for the higher temperatures (120 °C and 180 °C). This is in qualitative agreement with the view that most of the mobile components in the original coal are extracted by pyridine. As we will see later in the discussion below, this kind of simple interpretation may not be entirely correct. We will see that the dipolar-dephasing behavior of the residue may be better explained by a structural change in the entire coal (not just removal of mobile species) after pyridine extraction. One can assume that the inter-chain distances and void space in coals are dramatically increased with pyridine saturation. According to this more recent view, after removal of small trapped molecules and pyridine from the large void spaces, upon drying, a new structure is formed in the dried residue. In the dried residue, macromolecular chains and aromatic rings on the macromolecular network may get closer to each other after the collapse of the

large void spaces formed during swelling. In fact, the dipolar-dephasing behavior of the aromatic component of the extraction residue of coal 601 is very similar to that of the high rank LVB coal 501.

To get a better understanding of the relationship between molecular dynamics and the extractable components in coals, we examined the pyridine-saturated residue of coal 601 via ^1H CRAMPS. Figure 1D shows a set of dipolar-dephasing spectra of this sample obtained at 25 °C; the corresponding spectrum of the pyridine-saturated original coal 601 is shown in Figure 1C. There is an extra peak at about 4.7 ppm in the ^1H CRAMPS spectrum of the pyridine-saturated residue (Fig. 1D), compared to the spectrum of the pyridine-saturated original coal (Fig. 1C). This additional peak may be due to water absorbed in the residue (a hypothesis under examination).

The dipolar-dephasing behavior of the very mobile phase in the pyridine-saturated residue and in the pyridine-saturated original coal are different from each other. For Both samples, we can use two Lorentzian decay components to model the dipolar dephasing curves. The quantitative results based on this model are listed in Tables 3 and 4.

As discussed in previous reports, most of the very mobile components (dephasing time constant $> 150 \mu\text{s}$) in a pyridine-saturated coal are extractable. As shown in Figure 1D, there are still some very mobile components left in the pyridine-saturated residue; these components were clearly not extracted! As shown in Table 4, for a measuring temperature of 90 °C, the fraction of the very mobile (Lorentzian) components in the residue is about 23%, much lower than for the original coal (55%). Based on these two fractions, we can calculate the fraction of extractable component in the original coal 601 as 41%, which is consistent with the fact that the pyridine extractable fraction of coal 601 is around 40%. This suggests that these very mobile components in the original

coal are only partially (41%) extractable. The portion of these mobile components that are not extractable may be assigned as extremely mobile side chains or small molecules that are "tethered to" the rigid macromolecular network through probably only one covalent bond.

We can also see in Figures 1C and 1D that the ratio of aliphatic to aromatic components in the spectra with a dipolar dephasing time longer than 180 μ s is much lower for the pyridine-saturated residue than for the pyridine-saturated original coal. This is because the aliphatic components in the very mobile phase are preferentially extracted by pyridine.

For the pyridine-saturated original coal, aliphatic and aromatic components in the very mobile phase decay at almost the same rate (see Figure 1). However, the fastest decaying aliphatic component in the pyridine-saturated residue decays much faster than the aromatic component, as shown in Tables 3 and 4. This can be explained as follows. In the pyridine-saturated original coal, most of the very mobile components are liquid-like and have high translational mobility. *A priori*, some of them may serve as "spin diffusion bridges" between the protons of the rigid, macromolecular framework, and protons of the most mobile components. However, in the pyridine-saturated residue, the swelling or expansion of the macromolecular network leads to increased mobility of the very mobile components. The flexible side chains and/or tethered small molecules are still pretty much localized in the vicinity of their integral position and the extracted "spin diffusion bridges" are absent, so they cannot effectively exchange their magnetization through spin diffusion.

Comparing the results between Tables 3 and 4, we can see how temperature affects pyridine extraction. The fractions of the very mobile components in the residue do not change much when the temperature is increased from 25 °C to 90 °C. This suggests that the energy barrier that

restricts the motion of the very mobile components in the residue is well below kT at room temperature (i.e., 0.6 kcal/mole). However, the fraction of the mobile component with a dephasing time constant of 11 ms in the original coal 601 is increased from 18% to 28%, when the temperature is increased from 25 °C to 90 °C.

These results suggest the following pyridine/coal interaction mechanism. When pyridine molecules penetrate into the macromolecular network of the original coal, the relatively weak secondary (non-covalent) interactions between macromolecular chains are broken. This causes significant swelling or expansion of the macromolecular network of coal. The small molecules that are tightly confined in small voids in coal are released and become the major component of the very mobile phase in pyridine-saturated coal. When the temperature is increased from 25 °C to 90 °C, the kinetic energy and mobility of pyridine molecules are significantly increased. Therefore, pyridine molecules break more secondary interactions and more trapped small molecules are mobilized at higher temperature. That is why the fraction of the very mobile phase in the original coal 601 is significantly increased at higher temperature. As the very mobile phase in the pyridine-saturated residue consists mainly of mobile side chains and/or small "tethered" molecules, the temperature increase will not significantly affect the amount (fraction) of the very mobile phase.

As shown in Table 2, the fraction of relative mobile phase (slow Gaussian, dephasing time constant: 40 - 60 μ s) in the aromatic component of the original coal 601 is much higher than that in the aliphatic component at a temperature of 120° C or higher. This means that aromatic components are more mobile at higher temperature for coal 601. But the aliphatic component is predominant in the pyridine extract, so it seems that the NMR dynamics information on the original coal is contradictory to the pyridine extraction result.

Similar results have been found in previous ^{13}C and ^1H NMR studies of this group and other groups around the world, and have been a mystery in the literatures for years.

Our ^1H CRAMPS studies described in our previous reports and in this report clearly have solved this puzzle. To understand this phenomenon, we need to know first that we should not use the molecular dynamics information obtained on the original coals to explain any results from pyridine extraction experiments directly. Our studies clearly show that the relatively mobile components in the original coal are not necessarily pyridine extractable components. The 3-D macromolecular network in coals is dramatically changed by pyridine saturation. Very tightly confined small molecules, which may actually belong to the rigid component in the original coals, can be released during coal pyridine swelling and become very mobile -- thus extractable by pyridine. This explains why the aliphatic component is predominant in the very mobile phase of the residue after pyridine saturation. So, pyridine extraction results can be correctly understood only by molecular dynamics information obtained spectroscopically on pyridine saturated coals, e.g., from an NMR study like that shown in this report. Thus, the variable temperature ^1H CRAMPS results obtained on original coals and pyridine extraction residues provide some new insight into the molecular/macromolecular structure and dynamics of coals.

We are now changing our research emphasis to the in-situ ^1H CRAMPS study of coal in the temperature range of 250 °C - 500 °C. We are currently trying to increase the upper temperature limit of ^1H CRAMPS probe to about 500 °C using RF heating techniques.

Figure 1. The dipolar dephasing spectra of coal 601 obtained at 25 °C. (A) the original coal 601; (B) pyridine extraction residue of coal 601; (C) pyridine saturated original coal; (D) pyridine saturated extraction residue.

Table 1. *Dipolar dephasing data of dried pyridine-extraction residue of Coal 601.^a*

		Fast Gaussian		Slow Gaussian	
		percentage%	time(μ s)	percentage%	time(μ s)
25 °C	Aliphatic	94	10	6	46
	Aromatic	100	15		
120 °C	Aliphatic	89	10	11	73
	Aromatic	91	16	9	70
180 °C	Aliphatic	80	11	20	76
	Aromatic	77	13	23	46

a. There are no Lorentzian decay components for this sample.

Table 2. *Dipolar dephasing data for original coal 601.^a*

		Fast Gaussian		Slow Gaussian	
		percentage%	time(μ s)	percentage%	time(μ s)
24 °C	Aliphatic	89	10	11	33
	Aromatic	100	16		
120 °C	Aliphatic	81	9.0	19	54
	Aromatic	49	3.9	51	56
180 °C	Aliphatic	65	13	35	62
	Aromatic	34	8.5	66	44

a. There are no Lorentzian decay components for this sample.

Table 3. *Dipolar dephasing data of the very mobile components in the pyridine saturated extraction residue and original coal 601 at 25 °C.^a*

	Fast Lorentzian		Slow Lorentzian	
	percentage%	time(ms)	percentage%	time(ms)
original coal	26	0.23	18	9.5
aliphatic part in the residue	8.8	0.16	3.2	4.1
aromatic part in the residue	6.5	0.17	3.6	11

a. Fast-decaying (Gaussian) components are not shown here.

Table 4. *Dipolar dephasing data of the very mobile components in the pyridine saturated extraction residue and original coal 601 at 90°C.^a*

	Fast Lorentzian		Slow Lorentzian	
	percentage%	time(ms)	percentage%	time(ms)
original coal	27	0.17	28	11
aliphatic part in the residue	8.1	0.21	4.9	4.5
aromatic part in the residue	6.1	0.20	3.7	17

a. Fast-decaying (Gaussian) components are not shown here.

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